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Oregon Agricultural College
EXPERIMENT STATION

A REPORT OF

Chemical Investigations

ON THE

Lime-Sulfur Spray

By
H. V. TARTAR

Corvallis, Oregon

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*Resigned March 31, 1914.
†Elected Director of the Experiment Station and Dean of the School of Agriculture, April 8, 1914.

INTRODUCTION.

It is the purpose of this bulletin to present the greater part of the work carried out in this laboratory on the chemistry of the lime-sulfur solution. This work was begun in 1909, at the suggestion of Professor A. B. Cordley, who at that time was entomologist of this station, and carried on intermittently until October, 1913. The investigation was made under the Adams Act of the United States Government, an act which provides for scientific investigations by the agricultural experiment stations.

Reports of progress have been made, from time to time, in the Journal of Industrial and Engineering Chemistry and the Journal of the American Chemical Society. The entire completed results, however, and the conclusions therefrom, are presented here for the first time.

The work has been directed along those special lines which a thorough study of the literature indicated to be of most value, from the standpoint of the chemist. The results of the investigations naturally fall under four different heads: (1) The chemical composition of the lime-sulfur solution, (2) the chemical reaction between calcium hydroxide and sulfur in heated aqueous solution, (3) the theoretical basis for the proportions of lime and sulfur used in the commercial preparation of lime-sulfur, and (4) the methods of valuation as an insecticide.

Acknowledgement. The results given in Chapter I were obtained while Professor C. E. Bradley was chief chemist of this station. The subject matter of this chapter, in practically the same form as it is given here, was published in 1910 by Professor Bradley and the writer in the Journal of Industrial and Engineering Chemistry. Due acknowledgement is made to Professor Bradley for proposing the investigation, and for his suggestions, interest, and assistance during the early part of its progress.

CHAPTER I.

The Composition of Lime-Sulfur Solution.

The literature on the composition, properties, and use of the commercial lime-sulfur spray solution, now so widely employed as an insecticide and fungicide, consists largely of the details of field experiments which have been carried out in various localities by entomologists and horticulturists. In the majority of these tests but little attention has been given to the composition of the spray. The solution has been made by boiling in water, either by direct heat or with live steam, sulfur and freshly slaked lime. These materials have been used in varying proportions. In some instances the quantity of lime and of sulfur used, together with the specific gravity of the resulting solution, have been stated. Other than this, it has been the prevailing practice to give but little attention to the composition of the spray, and up to the present time there have been no definite systematic field experiments to show the relative insecticidal and fungicidal value to its constituents. The real chemical investigations dealing directly with the lime-sulfur solution have been carried out by Avery, Haywood, Thatcher, Giboney, and Wellington. (*)

Avery (1) modified standard methods of analysis to suit the conditions so that the total sulfur and total lime could be determined.

Haywood (2) was the first investigator to point out the real constituents of the spray solution now in use. He showed that it contained considerable amounts of polysulfides and thiosulfate, and but small quantities of sulfate and sulfite of calcium. A small amount of calcium hydroxide was supposed to be present. It may be stated here that the compounds which are formed when sulfur and calcium hydroxide are boiled in aqueous solution had been quite thoroughly investigated by Divers (3) and others previous to Haywood's work on the commercial spray solution. Standard methods of analysis were modified by Haywood so that quantitive estimations could be made of the sulfur combined as sulfides and polysulfides, as thiosulfate, as sulfate and as sulfite, respectively. The presence of sodium chloride was found not to affect the composition nor the amount of the sulfur compounds in the solution. Different formulas for the preparation of the spray were tried and the use of 1 part of lime to 1¼ parts of sulfur was suggested for practical purposes. Solutions made from commercial materials were found to be of the same composition as those made from chemically pure materials. One hour of cooking was demonstrated to be sufficient time to effect the combination of the sulfur with the lime.

Perhaps the most valuable part of Haywood's work was his study of the decomposition of the spray by the use of artificial experiments

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(1) Figures refer to references at end of chapter.

(*) Note. This chapter was written previous to publication of the work of Van Slyke (Bull. 329 N. Y. Agr. Exp. Sta., Geneva), Stewart (Bull. 99 Penn. Agr. Exp. Sta.), Harris (Tech. Bull. 6, Mich. Agr. Exp. Sta.) and Shafer (Tech. Bull. No. 11, Mich. Agr. Exp. Sta.)

approximating the conditions on the tree. He found that the principal immediate products of decomposition were calcium thiosulfate and free sulfur, and that the thiosulfate gradually decomposed to form sulfite and liberate more sulfur. The calcium sulfite finally oxidized to the sulfate. From the results obtained, a theoretical explanation of the action of the wash on insects was made. Haywood also suggested the preparation of a spray in which sodium hydroxide was substituted for slaked lime.

Thatcher (4) showed previous to Haywood that sodium chloride did not affect the quantity of sulfur compounds in solution. Later (5) Thatcher demonstrated that 1 part of lime to 1.95 parts of sulfur was the proper proportion of chemically pure materials to be used. The present extended commercial use of 1 part of lime to 2 parts of sulfur in the preparation of the spray attests the correctness of Thatcher's conclusion. In 1908 (6) he endeavored to work out the exact reaction between lime and sulfur when boiled in aqueous solution. His results indicated that perhaps the following primary reaction takes place:

$$3Ca(OH)_2+12S=CaS_2O_3+2CaS_5+3H_2O.$$

The analysis of concentrated lime-sulfur spray solutions seemed to show that a secondary reaction occurs in which the amount of thiosulfate decreases while the polysulfides increase. Thatcher made some suggestions regarding the nature of this reaction but, because of the lack of sufficient analytical methods, was unable to present any definite results.

Giboney, (7) from the results of laboratory experiments, suggested that 40 minutes is the proper length of time for boiling the solution. He also gave analytical methods for estimating the "sulfide" and "polysulfide" sulfur in the polysulfides. Prolonged boiling was found to effect the solution of a little more calcium and thus cause the formation of somewhat lower sulfides. Giboney also demonstrated the harmful effects of magnesia on the composition of the solution and pointed out the necessity of using lime which is comparatively free from this substance.

Wellington (8) stated that lime-sulfur-salt wash contains 25 per cent. to 30 per cent. of calcium monosulfide and hydrosulfide collectively. This view has not been upheld by any other investigator and is, no doubt, erroneous. Wellington, assisted by Fernald, showed, however, by field experiments, that calcium thiosulfate does possess some insecticidal value.

Experimental.

At the outset it soon became evident that some additional analytical methods must be devised which would enable one to ascertain more definitely the nature and composition of the polysulfide and also to estimate the calcium hydroxide which might be present.

It is a well-known fact that when an acid is added to a metallic polysulfide, sulfur equivalent to form the monosulfide of the metal

is liberated as hydrogen sulfide, while the remainder of the sulfur is deposited as free sulfur; e. g.,

$$CaS_4 + 2HCl = CaCl_2 + H_2S + 3S$$

For the sake of convenience, the sulfur equivalent to form the monosulfide is here spoken of as "sulfide" sulfur, while the remainder is spoken of as "polysulfide" sulfur. It can be readily seen that when the amount of "sulfide" and "polysulfide" sulfur are known, the simplest formula of the polysulfide can be easily calculated.

Method for "Polysulfide" Sulfur. Measure 10 cc. of the clear lime-sulfur solution into a 100 cc. volumetric flask and make up to the mark. For analysis 10 cc. aliquots are used. The aliquot is placed in a small beaker and about 30 cc. of distilled water is added. Tenth-normal hydrochloric acid is then run from a burette into the solution, drop by drop, with constant stirring until the yellow tint has practically disappeared. Two drops of methyl orange indicator is then added and the addition of the acid continued until the first permanent pink tint appears. (After standing for some time this tint will gradually disappear.) The solution will be milky white from the finely divided sulfur present, but it is not difficult to ascertain the exact end point of the reaction. After the solution is allowed to stand a few moments to permit the sulfur to settle and collect together, the sulfur may then be filtered on a weighed Gooch crucible, thoroughly washed, dried at a low temperature (about 40°) and weighed directly as free sulfur. It has been found somewhat more accurate to filter the sulfur on a small filter paper and, after thoroughly washing, gently boil the paper and its contents in 50 cc. of 10 per cent. potassium hydroxide solution until all the sulfur is dissolved. Upon cooling, 50 cc. of a 3 per cent. solution of hydrogen peroxide free from sulfates is added. Heat on the steam bath for exactly 30 minutes and then acidify with hydrochloric acid, precipitate with barium chloride in the usual manner in boiling solution, and finally weigh as barium sulfate.

The precipitation of the sulfur by means of the weak acid does not decompose the thiosulfate in solution.

Method for "Sulfide" Sulfur. For the determination of "sulfide" sulfur a well-known analytical method (9) has been but slightly modified. Because of the manner of manipulation, however, it is deemed advisable to give it in detail. As it is used here, the zinc is not precipitated as the normal sulfide, but as the polysulfide.

An ammoniacal zinc chloride solution is prepared by dissolving 3.2625 grams of pure zinc (or 4.0685 grams of pure zinc oxide is somewhat more convenient for use) in hydrochloric acid, supersaturating with ammonia and diluting to 1 liter. Each cc. of the solution is equivalent to 0.0016 grams of sulfur, or, in other words, it is a decinormal solution.

Measure 10 cc. of the clear lime-sulfur solution into a 100 cc. volumetric flask and make up to the mark. Use 10 cc. aliquots for analysis. The zinc solution is run in from a burrette until the filtered solution is colorless and no dark color is shown when a drop is brought in contact with an almost saturated solution of nickel sulfate spread

in drops on a white porcelain tile. This titration will give the approximate endpoint of the reaction. Several aliquots (four or five) are then placed in beakers and a series of determinations made by adding to the first the exact amount of zinc solution required in the above titration; to the second adding 0.2 cc. less of the zinc solution; to the third, 0.4 cc. less, and so on. These should be then allowed to stand about 30 minutes to insure complete precipitation of the zinc. The aliquots are then filtered. The amount of zinc solution which just suffices to remove all of the yellow color so that the resulting filtrate is colorless, is the correct titration. The great tinctorial power of the polysulfide serves adequately as an indicator in this determination.

The writer has been able to attain an accuracy of within 0.2 cc., or 0.0003 gram of sulfur, which is as close as could be determined gravimetrically.

For greater accuracy, larger aliquots (say 20 cc.) may be taken for the final titrations.

Method for Calcium Hydroxide. Attempts have been made to devise a method for the direct determination of the hydroxide by the use of a copper or zinc salt as suggested by Bloxam [10] in his work on ammonium polysulfides. None of these have been successful.

The amount of calcium hydroxide in the lime-sulfur solution may be calculated, however, from the data obtained in the above described methods for the determination of "polysulfide" and "sulfide" sulfur. The amount of tenth-normal acid used in the precipitation of the sulfur in the first method is the amount necessary to react with both the polysulfide and the hydroxide present, while the number of cc. of zinc solution used in the "sulfide" sulfur method is the decinormal titration of the polysulfide only. The difference between the two titrations will represent the amount of tenth-normal acid required to neutralize the hydroxide.

The final titrations with the zinc solution in this determination should be made on 20 cc. aliquots.

Results of Analyses. The analytical methods devised by Haywood [2] and Avery [1] have been used somewhat extensively during this investigation and have been found to be quite satisfactory. Some of the analyses made by the use of Haywood and Avery's methods in conjunction with our own are given in Table I. The solutions are representative, consisting of commercial samples, together with samples prepared in the laboratory by the use of different formulas and having different concentrations. Many other analyses have been made, but the general relationships found were the same as those here recorded and the analytical data are omitted to economize space. The results are calculated as grams per 100 cc. solution.

The laboratory samples were made by boiling the stated length of time, then allowed to cool, and after standing 12 hours, the clear supernatant liquid was drawn off into glass-stoppered bottles. Upon standing a day or two longer the analyses were made. In the case of samples No. 5 and No. 6, orange-red, needleshaped crystals separated out of the solution. A considerable excess of lime was used in the preparation of No. 5, and a slight excess in No. 6, and the crystals formed

Table I.

No.	History of sample.	Grams per 100 cc. original solution. Total CaO.	Sulfide sulfur.	Polysulfide sulfur.	Thio-sulfate sulfur.	Sulfite and sulfate sulfur.	Calcium hydroxide
1.	Commercial sample "Rex" lime-sulfur spray	12.12	5.92	23.06	1.47	0.08	None
2.	Commercial sample mfg. by Oregon Spray & Gas Co., Portland, Oregon	12.86	7.04	25.30	1.78	0.12	None
3.	Commercial sample mfg. by Niagara Spray Co., Hood River, Oregon	12.38	6.79	23.90	0.82	0.08	None
4.	Laboratory sample made by boiling 55 grams CaO, 110 gram sulfur, and 400 cc. of water under reflux condenser for 1¼ hours	9.49	3.93	14.82	2.98	None	None
5.	Laboratory sample made by boiling 55 grams, CaO, 55 grams of sulfur, and 450 cc. of water under reflux condenser 1 hour	4.99	1.80	6.25	2.43	None	Trace
6.	Laboratory sample made by boiling 60 grams, CaO, 110 grams sulfur, and 450 cc. water under reflux condenser 1 hour	9.45	3.60	12.43	3.84	None	None

were undoubtedly the oxysulfides of calcium. These compounds seem to be of variable composition, as they have been stated by various investigators to be $3CaO.\ CaS_4.\ 12H_2O$, $2\ CaO.\ CaS_3.\ 10$ or $11H_2O$, $5CaO,\ CaS_5.\ 20H_2O$, $4CaO.\ CaS_4.\ 18H_2O$, or $3CaO.CaS_3.\ 14$ or $15H_2O$.

The amount of calcium hydroxide in the clear spray solution is only a trace, if any. It appears that if there is hydroxide in the freshly prepared solution it either unites with some of the sulfur already in combination to form more polysulfide, or it unites directly with the polysulfides to form oxysulfides which crystallize out of the more concentrated solutions.

The spray solution is always alkaline. Its alkalinity must be due to the hydrolysis of the polysulfide as the thiosulfate is not hydrolyzed to any extent. Kuster and Heberlein (11) have found the sodium polysulfides to be strongly hydrolyzed in solution. The case of calcium polysulfide is analogous.

From Table I we are able to get an idea of the polysulfide. Thatcher (6) has stated unreservedly that the polysulfide is the pentasulfide. If this were correct, the amount of "polysulfide" sulfur would be exactly four times that of the "sulfide" sulfur. In nearly every instance our results show that the "polysulfide" sulfur is approximately 3½ times the amount of the "sulfide" sulfur, proving that the polysulfide in solution is not one compound only, but probably a mixture of the tetrasulfide and the pentasulfide of calcium.

The Absence of the Hydrosulfide. In order to establish thoroughly the above given "sulfide" sulfur method and tabulated results, it is necessary that the absence of the hydrosulfide should be proved. Wellington (8) and others have suggested the presence of this compound.

Divers and Shimidzu (3) showed that calcium hydrosulfide reacts very rapidly with sulfur to form polysulfide and liberate hydrogen sulfide, the action being as brisk as that of a strong acid with marble. When a solution of the hydrosulfide is heated with sulfur on a water bath the reaction is complete, only a trace of hydrosulfide remaining. Since free sulfur is always present in the preparation of lime-sulfur solution, it is improbable that the hydrosulfide could be present in appreciable quantity.

Divers and Shimidzu (3) employed a manganous salt for the detection of basylous hydrogen, the test being based upon the following reaction: $Ca(SH)_2+MnSO_4=CaSO_4+MnS+H_2S$, half of the sulfur present being liberated as hydrogen sulfide. Similar tests on the lime-sulfur solution with manganese sulfate have failed to reveal the presence of any hydrosulfide.

Again, when the spray solution is dried in hydrogen over sulfuric acid, hydrogen sulfide would be liberated by the decomposition of any hydrosulfide which might be present. Only the merest trace of hydrogen sulfide has been found to be liberated under these conditions.

In the "sulfide" sulfur determination, any hydrosulfide would in all probability be precipitated as zinc hydrosulfide; and, since it is calculated as the normal sulfide, only one-half of the sulfur present

as hydrosulfide would be shown by the titration with the zinc solution. A comparison of the amount of "sulfide" sulfur found by this method with the amount of sulfur which could be liberated from the solution as hydrogen sulfide was made. The determination of the hydrogen sulfide was effected by adding exactly enough tenth-normal acid to react completely with the sulfides present and by passing the gas liberated into an ammoniacal zinc chloride solution. The zinc sulfide thus obtained was digested in a small amount of concentrated potassium hydroxide solution, oxidized with hydrogen peroxide, and precipitated in the usual manner as barium sulfate. The comparative results of one of the determinations made in this way are as follows:

By "sulfide" sulfur method, 3.42 grams sulfur per 100 cc.

Sulfur liberated as H_2S, 3.44 grams sulfur per 100 cc.

If the hydrosulfide were present in any quantity, there would be found an appreciable difference in the amounts of sulfur obtained by the two different methods. No such difference has been found in the determinations made.

From the above data it may be said that only a trace of hydrosulfide, if any, is present in the lime-sulfur solution. What little there may be is perhaps that which might be formed by the hydrolysis of the polysulfide.

The Nature of the Polysulfide. When the spray solution is brought in contact with benzene or with chloroform, sulfur is extracted in considerable amount. This fact led to a rather extended study of the polysulfides; for it seemed that some of the sulfur was held in very feeble combination if not in physical solution. An endeavor was made to ascertain just the exact amount of sulfur which could be extracted from a definite quantity of the spray solution. Preliminary tests showed that carbon disulfide cannot be used for making such an extraction because it reacts rapidly with the polysulfide to form a thiocarbonate.

Small quantities (5 and 10 cc.) of the solution were shaken in separatory funnels with benzene and with chloroform, the solvent in each instance being removed occasionally and new quantities added. The combined extractions made by the two solvents respectively were then distilled and residual sulfur determined. A considerable quantity of sulfur was obtained from both the chloroform and the benzene extraction. A definite end-point to the extraction could not be obtained, however, for even after several days' extraction some sulfur continued to be gradually dissolved. Upon investigation, it was found that during the extraction an oxidation of some of the polysulfide to the thiosulfate had occurred, due to the contact with air in the separatory funnel, and some of the free sulfur was constantly liberated by this reaction. A very small amount of calcium carbonate was formed from the carbon dioxide present.

An extraction apparatus similar to that devised by A. H. Fiske ([12]) was arranged so that a quantity of the lime-sulfur solution could be extracted with benzene without coming in contact with the air. An extraction was made using 10 cc. of lime-sulfur solution. At the be-

ginning, a much larger quantity of sulfur was extracted than near the close of the experiment, which required several days' time. A definite end-point to the extraction could not be obtained and an examination of the extracted solution showed that there had been a considerable increase in the amount of thiosulfate, besides the formation of a very small quantity of what appeared to be calcium carbonate. The experiment was repeated, using 5 cc. of lime-sulfur solution diluted with 5 cc. of water. The details were carried out much more carefully than in the previous trial, but the results were the same. It was evident that either the benzene absorbed enough oxygen and carbon dioxide from the air in the apparatus to affect the composition of the solution or else there had been a decomposition of the polysulfide with the formation of more thiosulfate as well as small amounts of other products.

Previous to the benzene extraction described above an attempt was made to evaporate some of the lime-sulfur solution in partial vacuo, extract the dried residue with some sulfur solvent and ascertain what definite polysulfide, if any, remained. An experiment was tried drying 10 cc. of the solution in partial vacuo over calcium chloride. The quantity of thiosulfate increased enormously during the evaporation, indicating that an oxidation of the polysulfide had taken place.

Drying the solution in hydrogen sulfide was next tried, but the gas reacted rapidly with the solution, precipitating sulphur and forming hydrosulfide of calcium.

It was found after many trials that the solution could be successfully evaporated in pure hydrogen over sulfuric acid. Because of the conflicting data on the polysulfides in general, the details of the following experiments are given quite fully:

A lime-sulfur solution was made by boiling 55 grams of calcium oxide, 110 grams of sulfur and 450 cc. of water under a reflux condenser for one hour. Pure hydrogen was prepared from pure zinc and dilute sulfuric acid, and was washed, first with a potassium permanganate solution, then with a saturated solution of mercuric chloride, and finally with a strong solution of potassium hydroxide. The hydrogen was dried by passing it first through a calcium chloride tube and then through sulfuric acid.

Ten cc. of the lime-sulfur solution was placed in each of three glass mortars, which were immediately placed over sulfuric acid in different desiccators, and hydrogen passed into each until all traces of air were removed. The desiccators were then stoppered tightly, placed in a dark room where the temperature did not rise above 16°, and the solutions allowed to dry for three weeks. During this time the sulfuric acid became slightly turbid, indicating that a trace of hydrogen sulfide had been liberated. The dried residues had a light yellow color and contained some crystals of thiosulfate. Before the desiccators were opened, the hydrogen in them was tested and found to be practically pure. The dried residues were then removed, one by one, and immediately covered with pure, freshly distilled, dry carbon disulfide, previous tests having shown that this substance does not re-

act with the dried material. The residues were ground to a fine powder while still under the solvent. The carbon disulfide was then decanted off and the residues carefully washed with a fresh supply. That a considerable amount of free sulfur was extracted was certain from the yellow color of the solvent after the extraction. The powdered residues were then transferred to wide-mouthed glass-stoppered bottles and covered with more carbon disulfide. Long standing failed to extract any more sulfur. After the solvent was decanted off the residues were dried in a current of hydrogen and then analyzed. The analyses of the residues and the original material are given in Table II, the results being calculated as grams per 100 cc. original solution.

Table II.

		Grams per 100 cc. of original solution.					
No.	Sample	Total CaO.	Thio-sulfate sulfur.	Poly-sulfide sulfur.	Sulfide sulfur.	Sulfate and sulfite sulfur.	Sulfur extracted with CS_2.
1.	Original solution	9.68	3.39	15.05	3.85	None	.....
2.	Dried Residue (1)	9.25	3.43	3.64	3.58	None	11.25
3.	Dried Residue	9.52	3.71	3.82	3.72	None	11.21
4.	Dried Residue	Lost	3.84	4.43	3.60	None	10.28

(1) A small amount of residue No. 2 was lost after the extraction with carbon disulfide had been made, hence the low results on lime, etc.

The following described experiment was repeated using a lime-sulfur solution made by boiling 60 grams of lime, 110 grams of sulfur, and 450 cc. of water under a reflux condenser for 2½ hours. The method of procedure was the same with the exception that a fresh supply of hydrogen was passed into the desiccator every day or two in order to keep the supply pure and also to remove all traces of hydrogen sulfide which might be liberated. The results, calculated as grams per 100 cc. original solution are given in Table III:

Table III.

	Grams per 100 cc. original solution.					
Sample	Total CaO.	Thio-sulfate sulfur	Poly-sulfide sulfur.	Sulfide sulfur.	Sulfate and sulfite sulfur	Sulfur extracted with CS_2
Original solution	8.24	1.41	14.71	4.16	None	.....
Dried Residue	8.11	1.76	3.70	4.00	None	11.05

From the results given, it appears that there is a more stable, primary polysulfide of calcium. Although the analyses given do not permit of a definite statement regarding its composition, it does correspond, however, very closely to the formula CaS_2. The slight variability in the results obtained may be due to the fact that some of the higher polysulfide may not have been entirely decomposed in some instances. The writers have not found any indication whatsoever of the presence of the monosulfide in the dried residue.

Other investigators have found similar cases. Bloxam [13] discovered that of the potassium polysulfides, there was a more stable one having the formula K_4S_5. Kuster, [11] in his work on the sodium sulfides, found that after the polysulfide Na_2S_4 is formed the remainder of the sulfur in solution is not so firmly combined.

This lower primary polysulfide of calcium is amorphous, and mustard-yellow in color. It is readily soluble in water and in 95 per cent. alcohol. When dry, it is stable in the air.

An attempt was made to separate the polysulfide from the thiosulfate in the dried residue by the use of a solvent which would dissolve only the polysulfide. Trials were made using 80 per cent., 90 per cent., 95 per cent. and 98 per cent. alcohol, respectively, as the solvent, but the thiosulfate was found to be somewhat soluble even in 98 per cent. alcohol. The polysulfide is not soluble in absolute alcohol. No solvent has been found which will effect the complete separation of the thiosulfate from the polysulfide. All efforts to prepare a pure solution of calcium polysulfide from which a residue free from thiosulfate might be obtained have been unsuccessful, some thiosulfate always being present, though in some instances in very small amount.

Viewed in the light of previous investigations, it seems evident that all of the sulfur found in the lime-sulfur solution must be in chemical combination. The latest extensive work on this question was done by Kuster and Heberlein on the sodium polysulfides [11]. These investigators state that the polysulfides are analogous to the polyiodides and are the salts of hydrogen sulfide acids of the formula $H_2S.Sx$. They found that the more sulfur present, the less the hydrolysis of the polysulfide. This fact is indicative of chemical combination; for, if after a certain definite polysulfide is formed the remainder of the sulfur is simply in physical solution, there would be but little change in the amount of hydrolysis after enough sulfur had been added to form the primary compound.

These experiments with the polysulfide reveal a fact of practical significance in regard to the spray. It is not necessary for the polysulfide to oxidize in order that free sulfur be deposited, as has heretofore been stated. If the polysulfide is not oxidized completely before the spray dries on the tree, there will be left a lower polysulfide and some sulfur will be deposited which is not the result of oxidation. A considerable amount of the sulfur in lime-sulfur solution is in very feeble combination, and for the practical purposes to which it is applied might be considered as sulfur in physical solution.

Effect of Time of Boiling. Previous work on the lime-sulfur spray has shown that one hour is sufficient time for boiling in the preparation of the solution. Prolonged boiling has been found not to affect materially its composition. This latter statement has been found by us to be true only for certain conditions.

Solutions were prepared using different formulas and different lengths of time for boiling. The cookings were made under a reflux condenser and the samples were analyzed after standing 24 hours.

The results calculated as grams per 100 cc. original solution are given in Table IV.

Table IV.

No.	History of sample.	Grams per 100 cc. original solution. Total CaO.	Sulfide sulfur.	Polysulfide sulfur.	Thiosulfate sulfur.	Sulfate and sulfite sulfur.
1.	Boiled 55 grams lime, 55 grams sulfur, and 450 cc. of water for one hour	5.15	1.84	6.49	2.43	Trace
2.	Boiled 55 grams lime, 55 grams sulfur, and 450 cc. water for 2½ hours	5.10	1.82	6.32	2.45	Trace
3.	Boiled 60 grams lime, 110 grams sulfur, and 450 cc. water for 1 hour	9.45	3.60	12.43	3.84	Trace
4.	Boiled 60 grams lime, 110 grams sulfur, and 450 cc. water for 2¼ hours	8.39	4.16	14.71	1.40	Trace

In the case of samples No. 1 and No. 2, prolonged boiling did not affect the composition of the spray. With No. 3 and No. 4, where a larger proportion of sulfur was used, there was, however, a decided decrease in the amount of thiosulfate and an increase in the polysulfide present. There was also less lime in the solution. These results indicate that when the sulfur used is approximately double the quantity of lime, continued boiling does exercise a much more marked effect on the composition than when equal parts of lime and sulfur are used. The writer has been unable to furnish a complete, satisfactory explanation for the occurrence of this phenomenon. It may be said, however, that when the clear lime-sulfur solution is boiled, hydrogen sulfide is liberated in slight quantity, because of the hydrolysis of the polysulfide. As the hydrogen sulfide is liberated, a considerable deposit of calcium sulfite is obtained. The formation of the sulfite is due, no doubt, to the decomposition of the thiosulfate in the boiling solution.

Effect of Carbon Dioxide on Lime-Sulfur Solution. It has been conjectured by some that the carbon dioxide of the atmosphere may have an influence in the decomposition of the diluted lime-sulfur solution when sprayed upon the tree. Some work has been done by the writer to test out this point.

Pure carbon dioxide was passed into some of the concentrated lime-sulfur solution. A large quantity of hydrogen sulfide was rapidly liberated; apparently as much as if some strong acid were used. The following reaction occurs:

$$CaSx + H_2CO_3 = H_2S + CaCO_3 + Sx.$$

Two experiments were made by passing air through first a dilute lime-sulfur solution and then through a 10 per cent. solution of copper sulfate. Any hydrogen sulfide liberated would react to form copper sulfide in the latter solution. The air was passed through until the dilute spray solution no longer possessed a yellow color, the polysulfides present being completely decomposed. In one instance

the air was used directly and in the other the carbon dioxide was removed by passing through a potassium hydroxide solution.

There was a distinct precipitate formed where the normal amount of carbon dioxide was present. The precipitate, however, was quite small. The decomposed lime-sulfur solution had a strong odor of hydrogen sulfide. Paper moistened with lead acetate solution was gradually darkened, showing the presence of the gas.

In the instance when the air free from carbon dioxide was used there was only a trace of copper sulfide precipitated. The decomposed lime-sulfur solution had an odor of hydrogen sulfide. Evidently some hydrogen sulfide is formed during the oxidation, whether carbon dioxide is present or not, probably due to the hydrolysis of the polysulfide. The solution decomposed more rapidly when carbon dioxide was present, showing that it does exercise an influence in the decomposition of the spray, but the results indicate that this influence is comparatively small.

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CHAPTER II.

The Reaction Between Sulfur and Calcium Hydroxide in Aqueous Solution.

In connection with the investigations reported in Chapter I, the author looked up the literature relating to the reactions of the alkali and alkaline earth hydroxides with sulfur. It was found that all the work which had been done by various investigators was imperfect because of the faulty methods used for the examination of the solution containing the products of the reactions. The study of the literature showed, in fact, that the primary reaction of sulfur with any of the alkali and alkaline earth hydroxides, has never been determined.

While making the investigations reported in Chapter I, methods were developed which might also be used in studying the reaction between sulfur and any of the hydroxides mentioned. Because of the large commercial use of the reaction between calcium hydroxide and sulfur in the manufacture of lime-sulfur spray, a study of this reaction was considered.

Historical.

Fordhos and Gelis (1) concluded that, when sulfur is heated with a solution of potassium hydroxide, thiosulfate and polysulfide are formed. The results obtained indicated that the amounts of the different substances formed varies under different conditions.

Fahlberg and Iles (2) reported that when sulfur is melted with potassium hydroxide under certain conditions, polysulfide and thiosulfate are formed. When an excess of the alkali is present only sulfite and sulfate are produced.

In 1884, Divers and Shimidzu (3) found that calcium pentasulfide and thiosulfate are formed when calcium hydroxide and sulfur are boiled together in water. Later Divers (4) states that "at first the pentasulfide may be largely in excess of the thiosulfate, although it is not known to have been in such excess as the following equation requires:

$$3Ca(OH)_2+12S=CaS_2O_3+2CaS_5+3H_2O.$$

Senderens (5) studied the reactions of the oxides of the alkali and alkaline earth metals when boiled with sulfur and water. His results indicated that they react as represented by the following general equation:

$$3M''O+nS+XH_2O=2M''Sn\text{-}_2+M''S_2O_3+XH_2O.$$

He also found that with dilute solutions a greater amount of thiosulfate was formed from the decomposition of the polysulfide.

Pomeranz (6) supposed that the primary reaction between the alkali hydroxides and sulfur is analogous to that between the alkali hydroxides and chlorine in the cold, and takes place as represented in one of the following equations:

$$4NaOH+2S=Na_2SO_2+2H_2O,$$

or

$$3NaOH+2S=Na_2S+NaHSO_2+H_2O.$$

In support of this view, Pomeranz states that a mixture of sulfur and sodium hydroxide in the ratio 2S : 3NaOH has a similar bleach-

ing action on p-nitroaniline-red to that of sodium hyposulfite. He holds that the polysulfide and thiosulfate are only produced by the further reaction of sulfur on the sulfide and hyposulfite.

The work of Haywood, (7) Thatcher, (8) and Bradley and the author (9) show that the products formed by the reaction of sulfur with calcium hydroxide in heated aqueous solutions are calcium polysulfide and thiosulfate. Thatcher concluded from his incomplete data that the reaction in dilute solution might take place as indicated by the following equation:

$$3Ca(OH)_2+12S=CaS_2O_3+2CaS_5+3H_2O.$$

The author and Bradley showed that in solutions resulting from this reaction both calcium tetrasulfide and pentasulfide were present.

On the whole, the literature shows that the products formed by the reaction of sulfur with the alkali and alkaline earth hydroxides are polysulfides and thiosulfates. In practically all of the investigations, air was not excluded from contact with the products of the reaction. The neglect of this precaution introduced an error due to the rapid oxidation of the polysulfides. Again, most of the experiments were made using an excess of sulfur and, evidently, without thought of a possible secondary reaction of sulfur with the products formed by a primary reaction. Lastly, previous work has been handicapped because no methods have been available for determining the amount of the hydroxide of a metal present in solutions also containing polysulfides and thiosulfate of the same metal.

Methods of Analysis.

For the study of this reaction, methods are required for the determination of sulfur present in the form of polysulfides, of thiosulfate, of sulfite, and of sulfate; also for calcium combined as polysulfides, as thiosulfate, and as hydroxide.

The calcium in the form of thiosulfate and sulfur present as polysulfide, as thiosulfate, and as sulfite and sulfate were determined according to the methods outlined by Haywood. (7)

The determination of calcium combined as polysulfides was made by using the method for "sulfide" sulfur reported in Chapter I. The number of cubic centimeters of the ammoniacal zinc chloride solution required is the tenth-normal titration of the calcium combined as polysulfide.

Calcium hydroxide was also estimated by the method given in Chapter I.

Experimental.

The sulfur was purified by recrystallization from pure carbon disulfide in such a manner that a fine crystal meal was obtained. This was pressed free from the mother liquor and thoroughly dried at a gentle heat. It was finely ground in a mortar and sifted through an 80 mesh sieve just before using. The calcium hydroxide used in making the hydroxide was prepared by heating a sample of "J. T. Baker's Analyzed, C. P." calcium carbonate in a muffle furnace until it was competely converted into the oxide. The distilled water had been recently boiled to expel oxygen and carbon dioxide.

A serious difficulty which presented itself at the beginning was the easy decomposition of calcium thiosulfate, one of the products of the reaction, into calcium sulfite and sulfur in heated aqueous solutions. After some more or less unsuccessful work had been done, it was deemed advisable to make first a study of the reaction of sulfur with one of the alkali hydroxides (where there would be no decomposition of the products of the reaction) before proceeding further with the study of the reaction of sulfur with calcium hydroxide. With this idea in mind, an investigation of the reaction of sulfur with potassium hydroxide was carried out.

The results of this work have already been published ([10]) and it is unnecessary to discuss them further in this bulletin.

Further experiments, similar to those used in the case of potassium hydroxide, were tried; and it was found practically impossible to combine even small amounts of calcium hydroxide and sulfur without some decomposition of the thiosulfate produced. This decomposition occurs at temperatures much below 100° centigrade. After several unsuccessful attempts had been made it was decided to attack the problem from a different standpoint. This will be explained in what follows.

Two different solutions, each containing mixtures of calcium tetrasulfide, pentasulfide, and thiosulfate in different amounts, were prepared by boiling calcium hydroxide and sulfur in water. In each case, the sulfur was used in slight excess and the boiling continued for more than an hour. For convenience, these solutions are designated as solutions A and B. The analysis of a 20 cc. aliquot of solution A and a 25 cc. aliquot of solution B are given in Table I.

Table I.—Composition of Aliquots of Solutions Made by Boiling Calcium Hydroxide and Sulfur in Water.

Sample	"Sulfide" Sulfur	"Polysulfide" sulfur.	Thiosulfate sulfur	Total calcium (calculated as CaO)	Free calcium hydroxide	Sulfur combined as sulfite and sulfate
	grams	grams	grams	grams	grams	grams
20 cc. aliquot sol. A.....	1.256	4.714	0.360	2.56	none	none
25 cc. aliquot sol. B.....	0.866	3.178	0.936	2.42	none	none

A 20 cc. aliquot of solution A was transferred to a litre volumetric flask containing 800 cc. of an almost saturated solution of calcium hydroxide. The flask was then connected to a hydrogen generator and pure hydrogen passed in until all the air had been expelled, in order to prevent any oxidation of the polysulfide to thiosulfate. After the removal of the air, the body of the flask was almost wholly immersed in water which was maintained at a temperature near 70°C. The flask was kept in the water at this temperature for over two hours. During this time, it was gently shaken twice and a continuous stream of hydrogen passed in. Finally, the solution was allowed to cool, made up to

1000 cc. volume, and analyzed. For results see Experiment I Table II.

A second experiment, which was simply a duplicate of experiment 1, was carried out. The results are also given in Table II. .

In the third experiment a 25 cc. aliquot of solution B was transferred to a half litre volumetric flask containing 450 cc. of an almost saturated solution of calcium hydroxide. The flask was then handled in exactly the same manner as in Experiment 1, and the solution finally made to 500 cc. volume. The analytical data are given in Table II.

A duplicate of Experiment 3 was performed and the results obtained are given as Experiment 4 in the following table.

Table II.—Composition of Aliquots Containing Mixtures of Calcium Tetrasulfide and Pentasulfide After Being Heated in Solutions Containing Excess of Calcium Hydroxide.

	"Sulfide" sulfur. grams	Poly-sulfide" sulfur. grams	Thiosulfate sulfur. grams	Sulfate and sulfite sulfur. grams	Free calcium hydroxide grams
Exp. 1	1.456	4.312	0.520	none	present in excess
Exp. 2	1.467	4.286	0.510	none	present in excess
Exp. 3	0.977	2.960	1.030	none	present in excess
Exp. 4	0.981	2.919	1.025	none	present in excess

A fifth experiment was made in the following manner: Exactly 41.38 grams of calcium hydroxide (prepared by slaking 31.32 grams of calcium oxide with water) were placed in a Jena glass flask, 2 litres capacity. To this was added 59.4 grams of sulfur, which had been thoroughly wet, and enough distilled water to make the volume somewhat greater than 500 cc. The flask was then connected to a hydrogen generator as in the preceding experiments. The mixture of calcium hydroxide, sulfur, and water was then heated to boiling and let boil briskly for 40 minutes, when the combination of the calcium hydroxide and sulfur seemed to be complete. During this time the flask was frequently shaken and a continuous stream of hydrogen passed in. The flask was next disconnected and the hot solution obtained was filtered quickly through a glass wool plug into a litre volumetric flask, cooled, made up to volume, and analyzed. The results are given in Table III.

A duplicate of the preceding experiment was made and the results are recorded in Table III as Experiment 6.

Table III. Composition of Solutions Obtained by Boiling Calcium Hydroxide and Sulfur in Water.

	"Sulfide" sulfur grams	"Polysulfide" sulfur grams	Thiosulfate sulfur grams	Total calcium (calculated as CaO) grams	Free calcium hydroxide grams
Exp. 5	11.52	35.56	11.50	30.15	None
Exp. 6	11.55	35.41	11.49	30.27	None

Discussion of Results.

It will be noted that in the two solutions whose composition is given in Table I, the "polysulfide" sulfur is more than three times greater than that of the "sulfide" sulfur. If the polysulfide present

were simply the tetrasulfide (CaS_4) it would be exactly three times greater. Evidently, both the solutions contain a mixture of calcium tetrasulfide and pentasulfide (CaS_5).

The data given in Table II show that the "polysulfide" sulfur is, considering the experimental error of analysis, three times greater than the "sulfide" sulfur, indicating that the polysulfide present is the tetrasulfide. Since there was an excess of calcium hydroxide in each of these solutions, **it is evident that calcium tetrasulfide is the lowest polysulfide formed when calcium hydroxide and sulfur react in aqueous solution.**

Comparing the results given in Tables I and II, it will be seen that in Table II there has been an increase in the amounts of both the "sulfide" sulfur and the sulfur combined as thiosulfate. In each of the experiments, these forms of combined sulfur increased in equal amounts. The data presented show that the **"polysulfide" sulfur in the aliquots from solutions A and B, which was in excess of that required to form the tetrasulfide of the calcium combined as polysulfide, has reacted in experiments 1, 2, 3, and 4 with more calcium hydroxide.** The results from the experiments just enumerated also show that the primary reaction between calcium hydroxide and sulfur takes place as represented by the following equation:

$$3\ Ca(OH)_2+10S=2CaS_4+CaS_2O_3+3H_2O.$$

This reaction is analogous to that occurring with potassium hydroxide and sulfur ([10]) except that with the potassium hydroxide the trisulfide (K_2S_3) is formed.

In experiments 5 and 6 the calcium hydroxide and sulfur were used in amounts proportionate to those required in the equation given in the preceding paragraph. The analytical results show that there was but a slight loss of calcium and sulfur due to the formation of the more insoluble calcium sulfite. Since there was no uncombined hydroxide present, all of this substance had reacted with the sulfur. This fact, and the general relationships of the amounts of the different forms of combined sulfur with each other, confirm the conclusions drawn from the preceding experiments.

In solution A and B where an excess of sulfur was used in preparation, some calcium pentasulfide was present. This justifies the conclusion that a secondary reaction has taken place, in which sulfur has combined with the tetrasulfide to form the pentasulfide.

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CHAPTER III.

The Theoretical Basis for the Proportions of Lime and Sulfur Used in The Commercial Preparation of Lime-Sulfur Solution.

Various formulas (i. e., proportions of lime, sulfur and water) have been recommended for use in the preparation of the commercial lime-sulfur spray. In the early literature on this subject, the proportions of lime (CaO) and sulfur vary within wide limits; the more recent work (1) shows the proper ratio of lime to sulfur to be approximately 1 : 2. There are, however, some differences still existing among the recommendations made in this connection by the different agricultural experiment stations. It is well known, too, that various factors, such as concentration and length of time of boiling, have an influence on the amounts of lime and sulfur required. Even the time of cooling, following the boiling period, modifies the composition of the solution and consequently the requirements of raw material. For example, in one of the experiments at our local station plant where 108 gallons of material were prepared, a sample taken and immediately cooled just at the close of the cooking period had a gravity of 33 degrees Beaume, while one taken after the solution had cooled in the tank for 12 hours, had only a 30 degree strength. This decrease in gravity was due, no doubt, to the decomposition of calcium thiosulfate in the hot solution. Similar experiments, in which the entire solution was cooled immediately after boilng, showed no decrease in gravity upon standing. Because of these numerous factors which influence the composition of the spray, the formulas given by different investigators have been worked out largely by the "cut and try" method. Different methods of lime, sulfur, and water have been cooked for various lengths of time, and from the analyses made of the resulting solutions and sediment (sulfite), the formulas have been derived. But little, if any, attention has been given to the exact chemical reactions which occur.

To all familiar with this subject, it is very evident that any formula used in making lime-sulfur must necessarily be based on the reactions taking place. Investigations reported in Chapter II show that these reactions are those represented by the following equations:

(1) $3Ca(OH)_2+10\ S=2\ CaS_4+CaS_2O_3+3H_2O$

(2) $CaS_4+S=CaS_5$

(3) $CaS_2O_3=CaSO_3+S$

There is also some oxidation of the polysulfides when the material is exposed to the air, but this is so slight, under ordinary conditions of commercial preparation, where large, tall cooking vats are used, that it need not be considered here. The knowledge of the exact nature of these chemical reactions affords a theoretical basis for determining the proportions of lime and sulfur required in the preparation of a given sample of lime-sulfur. This will be brought out in the discussion which follows.

It will be seen from the equations given above that the compounds formed by the reaction between calcium hydroxide and sulfur, under ordinary commercial conditions of manufacture, are calcium tetrasul-

fide, pentasulfide, thiosulfate, and sulfite. All of these compounds are readily soluble in water with the exception of the sulfite, which is comparatively insoluble. This being true, the chemical analysis of the lime-sulfur solution shows the amounts of lime (slaked with water to form hydroxide) and sulfur that have reacted in the formation of the same, except the amounts of these substances necessary to form the insoluble sulfite produced. From the knowledge of the chemical reactions that occur, however, it is not a difficult matter to estimate, from the chemical analysis of the solution, the quantity of sulfite which has been formed. Equation (1) in the preceding paragraph shows that when calcium hydroxide and sulfur combine, one-third of the calcium is combined as thiosulfate and two-thirds as polysulfide. Since there is no decomposition of the polysulfide, the quantitive estimation of the calcium combined in this form gives a means for determining the amount of thiosulfate which has been formed. The difference between this total estimated amount of thiosulfate and the amount actually present in the solution, is the quantity that his decomposed; and from this data the amount of sulfite can be easily calculated. The initial ratio of lime to sulfur is also easily determined when one knows not only the amounts of calcium and sulfur present in a given lime-sulfur solution, but also the insoluble sulfite produced in the preparation of the same.

The analytical methods for determining the amounts of calcium combined as polysulfide, as well as the amounts of other constituents of lime-sulfur, have been very thoroughly worked out (2) and it unnecessary to discuss them here.

The actual application of the discussion given above is brought out in Table 1. The chemical composition of several samples of commercial lime-sulfur solution are given; also the estimated amounts of insoluble calcium sulfite formed and the calculated ratios of lime to sulfur. The results relating to chemical composition are expressed as grams per 100 cc. of solution.

Table I. Chemical Composition of Lime-Sulfur Solution: Also the Estimated Amount of Calcium Sulfite Produced, and the Calculated Ratios of Lime to Sulfur Required for Preparation.

Sample	Grams per 100 cc. of solution.							
	Specific gravity	Calcium combined as polysulfide (CaO)	Calcium combined as thiosulfate (CaO)	Estimated calcium combined as insol. sulfite (CaO)	Sulfur combined as polysulfide (S)	Sulfur combined as thiosulfate (S)	Estimated sulfur combined as insol. sulfite (S)	Ratio lime (CaO) to sulfur required
No. 1	1.2585	9.464	1.820	4.060	26.313	2.080	2.320	1:2.00
No. 2	1.3335	13.943	0.672	5.152	37.498	0.768	2.944	1:2.08
No. 3	1.2825	11.357	1.120	4.558	30.780	1.280	2.604	1:2.03
No. 4	1.2560	10.248	1.008	4.116	27.926	1.152	2.354	1:2.04
No. 5	1.2820	11.424	0.840	4.872	31.283	0.960	2.784	1:2.04
No. 6	1.3110	11.802	1.198	4.703	31.930	1.370	2.688	1:2.04
No. 7	not determined	10.834	1.286	4.131	28.980	1.470	2.360	1:2.01

The data given show that the proportion of lime (CaO) to sulfur which reacts in the preparation of the more concentrated commercial lime sulfur solutions, is but a mere trifle greater than 1 : 2. Unfortunately the author has not had opportunity to examine more dilute solutions prepared under commercial conditions. It is evident, however, from the work of Thatcher (3) and Van Slyke (1) that the ratio in this case would be somewhat greater than 1:2; in some cases it would be perhaps 1:2.25.

The theoretical basis given here will not exactly apply, of course, to the preparation of small amounts of solution, say 150 gallons or less. where the oxidation of the polysulfides occurs to a considerable extent through contact with the air.

Acknowledgment is due to Mr. R. H. Robinson who made several of the chemical analyses reported above.

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CHAPTER IV.

On the Valuation of Lime-Sulfur as an Insecticide.

At the present time, the object of the examinations made of samples of commercial lime-sulfur solution, in different chemical laboratories throughout the country, is to ascertain data regarding composition. In many cases, simply the total lime content, total sulfur content, and specific gravity are ascertained. Oftentimes, however, quantitative determinations are also made of the different forms of sulfur in combination. Entomologists and horticulturists, making field experiments, generally use a gravity test only.

A large proportion of the lime-sulfur used is for insecticidal purposes. Consequently, examinations made in the valuation of the same should be quantitive determinations of those properties from which the spray derives its insecticidal value. Actual chemical composition is a secondary matter except in so far as it may be an indication or measurement of these properties. For this reason, the determination of specific gravity is perhaps of little value except in a very general way. Samples of lime-sulfur having the same specific gravity may not be alike in chemical composition nor in many other properties. For example, a sample having a low specific gravity may have a greater per cent of polysulfides than a sample having a somewhat higher specific gravity.

In this discussion of valuation, it is well to consider first the properties which give to lime-sulfur its insecticidal value. The most exhaustive investigation available is, perhaps, that of Shafer. (1) He showed that with scale insects, like San Jose scale, the calcium polysulfides present in the solution soften the so-called wax about the margin of the insect, and, on drying, cause it to stick to the plant. In the cases tried, the insects stuck tightly enough to cause also the death of the young by sealing them under the scale covering of the mother. Shafer's work also strongly indicated that one of the principal, if not the principal, insecticidal effect of lime-sulfur solution, upon insects of the type mentioned, is its great power of absorbing oxygen, thus causing the treated insects to suffer because of an insufficient supply of this element. Other experiments made by Shafer showed that sulfur dioxide is not "formed in appreciable amounts from sulfur deposited by lime-sulfur except at temperatures much above those found under spraying conditions in the orchard." The liberation of this gas is, evidently, not in amounts large enough to make it of importance in any consideration of the insecticidal properties of the spray. The work done by the department of entomology of this station (2) indicates clearly that the principal insecticidal constituents are the calcium polysulfides. Experiments tried with calcium thiosulfate on San Jose scale (3) showed this material to have but little, if any, insecticidal value. Wellington (4) arrived at similar conclusions. Shafer's (1) results also indicated that the thiosulfate has a limited insecticidal efficiency.

It has been known for long, too, that with certain insects, free

sulfur has some killing power. It is stated that dry sulfur has been used in California perhaps a quarter of a century against almond red spider. The experimental work carried on by the experts of the California Agricultural Experiment Station (5) and the Bureau of Entomology, U. S. Department of Agriculture (6) shows that towards certain insects free sulfur has marked insecticidal properties.

There is also the possibility that hydrogen sulfide, a gas poisonous to insects, may be liberated from lime-sulfur when it combines with the carbon dioxide of the atmosphere or that given off in the breath of insects. So far as the writer knows, no means has been found to ascertain the extent to which this occurs. Experimental work carried out at this laboratory, however, indicates that if hydrogen sulfide is liberated under normal conditions, it is in very small quantity, and is evidently not an important matter to consider here.

From the discussion preceding, it appears that in general the insecticidal properties of lime-sulfur are due principally to the following-named properties:

(1) Its power to take up large amounts of oxygen, (2) its ability to soften the newly secreted wax at the margin of scale insects, and (3) the amount of free sulfur formed in its decomposition If this be true, then the question of the correct valuation resolves itself into the quantitative measurement of these factors.

The amount of oxygen consumed depends upon reactions as represented in the following equations:

$$CaS_5 + 3O = CaS_2O_3 + 3\ S$$
$$CaS_4 + 3O = CaS_2O_3 + 2\ S$$
$$CaS_2O_3 = CaSO_3 + S$$
$$CaSO_3 + O = CaSO_4$$

The combination of oxygen with the moist polysulfides is very rapid and quantities of the tetrasulfide or pentasulfide containing the same amount of calcium would absorb the same amount of oxygen and consequently produce the same amount of thiosulfate. This last named substance decomposes very slowly under ordinary conditions. For this reason, calcium sulfite is formed very gradually and the oxygen required to form the sulfate is absorbed slowly,—too slowly, in the writer's opinion, to make it of insecticidal importance. Investigations made by the entomologist of this station indicate that calcum sulfite has practically no insecticidal effect upon San Jose scale.

The oxygen required to convert the polysulfides present in a given solution into thiosulfate, can be easily estimated by the use of the methods of Harris. (7) The titration used in the determination of "monosulfide" (for explanation of this term see bulletin referred to) sulfur may be used in estimating the amount of oxygen which will combine with the polysulfide present to form thiosulfate. In this case, 1 cc. of tenth-normal iodine is equal to 0.0024 grams of oxygen. The writer suggests that this oxygen-consuming capacity might be expressed as the "oxygen number" (analogous to the iodine number of fats), this term meaning the amount of oxygen consumed expressed as

per cent. of lime-sulfur solution, or, in other words, the number grams of oxygen absorbed by 100 grams of lime-sulfur.

Free sulfur is liberated from lime-sulfur by reactions represented by the following equations:

$$CaS_4 + 3O = CaS_2O_3 + 2\ S$$
$$CaS_5 + 3O = CaS_2O_3 + 3\ S$$
$$CaS_2O_3 = CaSO_3 + S$$

Since the oxidation of the polysulfide takes place rapidly, there is a correspondingly rapid deposition of sulfur. The liberation of sulfur due to the decomposition of the thiosulfate is much less rapid. Considering everything, however, it appears that all of the sulfur liberated might be of equal insecticidal value; at least, there is no good evidence available to the contrary. The chemical estimation of the sulfur which will be deposited from a given amount of lime-sulfur solution can be made without difficulty. All of the sulfur present in the polysulfides in excess of that necessary to form the "monosulfide" of calcium combined in this form, would be deposited. So would one-half of the sulfur present as thiosulfate in the original solution. The chemical methods for making these determinations have already been worked out in a thorough manner ([7&8]) so that it is unnecessary to go into a detailed discussion of them here. The author suggests that the total free sulfur which would be deposited might be expressed as the "available sulfur number," this term meaning sulfur deposited expressed as per cent. of the original lime-sulfur solution.

The third insecticidal property mentioned above is not so easily estimated. In fact, it is not definitely known why the spray solution softens the wax on scale insects. It might be stated, however, that calcium thiosulfate is neutral in solution and gives no caustic effect on the hands, while solutions containing calcium polysulfide are very caustic. It is true that there is a small amount of calcium hydroxide in lime-sulfur solutions, due to hydrolysis of the polysulfide, but it is present in insufficient quantity to say that the caustic properties are due to the alkalinity of the solution. The writer's experience in handling the spray simply verifies the correctness of Shafer's statement that "the so-called caustic action of the wash on the hands seems rather due to its strong reducing power (power to absorb oxygen) than to the alkalinity of the solution." It is quite possible that this reducing power may also cause the softening of the so-called wax on the scale insects. If this be true, the "oxygen" number mentioned above would give its quantitative measurement. At any rate, the power of the spray to soften the so-called wax is evidently due to some property of the polysulfides; and in the light of present knowledge no definite statement can be made regarding its exact nature or its exact quantitative analytical measurement.

In conclusion, the writer wishes to state that the above discussion is merely a suggestion to chemists and entomologists. There may be other insecticidal properties of the spray than those mentioned, and it is possible that the ordinary methods of valuation now in use are the best. If not, the discussion given here may prove to be of some value.

List of References.

(1) Shafer; Tech. Bull. No. 11, Mich. Agr. Exp. Sta.
(2) Wilson; Unpublished results.
(3) Wilson; Biennial Crop Pest and Horticultural Report pg. 112 (1913)
(4) Wellington; Bull. 116, Mass. Agr. Exp. Sta.
(5) Bull. 154 and 234, Cal. Agr. Exp. Sta.
(6) Private correspondence.
(7) Harris; Tech. Bull. No. 6, Mich. Agr. Exp. Sta.
(8) Haywood; Jour. Amer. Chem. Soc. 27, 244 (1905)
(9) Tartar and Bradley; Jour. Ind. Eng. Chem. 2, 271 (1910)

SUMMARY.

(1) Simple and accurate methods have been perfected for the determination of the composition of the polysulfides and the amount of calcium hydroxide in lime-sulfur.

(2) Free dissolved calcium hydroxide is not a constituent of the lime-sulfur solution, its alkalinity being due to the hydrolysis of the polysulfide.

(3) The polysulfides in solution are probably a mixture of the tetrasulfide and pentasulfide of calcium.

(4) The tests made show the absence of hydrosulfide in appreciable quantities. Should any be present, it is that which might be formed by the hydrolysis of the polysulfide.

(5) There seems to be a more stable polysulfide of calcium, which the results indicate to be CaS_2, calcium disulfide.

(6) A considerable amount of sulfur in the solution is very feebly combined, and for practical spraying purposes may be considered as sulfur in physical solution.

(7) It is not necessary for the spray to oxidize in order that free sulfur may be deposited from the same.

(8) Prolonged boiling when approximately one part of lime and two parts of sulfur are used, causes a decrease of thiosulfate.

(9) Carbon dioxide reacts with lime-sulfur solution, liberating hydrogen sulfide. Laboratory experiments indicate that the carbon dioxide of the air may exercise some influence in the decomposition of the spray upon the tree.

(10) The primary reaction between calcium hydroxide and sulfur in heated aqueous solution takes place as represented by the following equation:

$$3Ca(OH)_2+10S=2\ CaS_4+CaS_2O_3+3H_2O.$$

(11) When sulfur is used in excess, a secondary reaction occurs, in which it combines with the calcium tetrasulfide to form the pentasulfide.

(12) The theoretical basis has been given for the proportions of lime and sulfur used in the commercial preparation of the lime-sulfur solution.

(13) New standards of valuation based upon insecticidal properties have been suggested.